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Review

Effect of silane and zirconia on the thermal property of cathodic electrophoretic coating on AZ31 magnesium alloy

Ruanli Zhu^{a,b}, Jin Zhang^{a,b,*}, Cheng Chang^a, Shuai Gao^a, Na Ni^{a,b}^a Beijing Key Lab. for Corrosion, Erosion and Surface Technology, University of Science and Technology Beijing, Beijing 100083, China^b Institute for Advance Materials and Technology, University of Science and Technology Beijing, Beijing 100083, China

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Abstract

Magnesium alloys, the lightest structural metal, are used in the field of aeronautics and astronautics more and more, however they are still limited for the poor corrosion resistant and high temperature property. In order to satisfy the need of long time store and short time operation at elevated temperature, coating with excellent corrosion resistance and thermal resistance was prepared on the surface of Mg alloy AZ31B. The cathodic electrophoretic deposition was applied for the preparation of coating. The bonding of organic electrophoretic deposition coating with substrate was improved using silane pretreatment. Nano-ZrO₂ powder treated by silane was added into electrophoretic deposition solution. The corrosion resistance property of electrophoretic coating was evaluated using Machu test, and thermal characteristic using the thermal shock experiment and DTA respectively. The morphology of the coating was examined by SEM. It is found that both the corrosion resistant and thermal shock resistant properties can be improved by modifying the Mg specimen with APS silane, while adding nano-ZrO₂ powder treated by GPS silane to the coating has the optimal effect. And the results also show that the main reason of the coating damage after thermal shock at 400 °C or 500 °C is mainly for the thermal stress.

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Keywords: Thermal shock property; Cathodic electrophoretic coating (E-coating); Silane treatment; ZrO₂

Magnesium alloy is the lightest engineering application metal, its application field has been extended from 3C electronic products, automotive components to the field of aerospace, especially in the later field, due to the properties of low density, good machining performance and electromagnetic shielding advantages. Combining with the lightweight

requirement, its usage would be more and more [1,2]. But it restrict its application in the field of aerospace for its poor corrosion resistance when storage and poor high temperature properties. At last years, a lot of research have been done to improve the two properties, one way is changing the Mg alloy self, such as adding some rare earths alloy elements, optimizing the microstructure and composition, and so on [3–9]. The other way is coating on the surface of magnesium alloy, such as YSZ coating [10] and organic coating [11,12].

Cathode electrophoresis is a low cost preparation technology, it can be used on complex metallic components and to prepare large area coating [13]. Although the preparation technology of cathodic electrophoretic coating used on magnesium alloy has good corrosion resistance [13,14], there are two shortcomings, the poor binding with substrate and heat property.

At the last few years, the new technology of silane surface treatment has both of good corrosion resistance and

* Corresponding author. Beijing Key Lab. for Corrosion, Erosion and Surface Technology, University of Science and Technology Beijing, Beijing 100083, China. Tel.: +86 15010921659.

E-mail address: zhangjin@ustb.edu.cn (J. Zhang).

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good adhesion between the coating and substrate [15,16]. The silane was deeply researched by Zhu Danqing [17], and the results show that the silane not only form a dense protective film with good corrosion resistance on the metallic surface, but also can improve the adhesion between organic coating and the metal (Al, carbon steel). The cathodic electrophoretic coating was studied on the magnesium alloy silane treated by Zhang Jin [14,18], and the results show that, via the silane treatment, not only the adhesion between the cathodic electrophoretic coating and the matrix was improved, but also corrosion resistance is improved significantly too.

And another interesting thing is that the corrosion resistance and heat resistance of organic coatings can be improved by adding some inorganic fillers [19–21]. the nano-ZrO₂ treated by aminopropyltrimethoxy silane is added to the epoxy. It is found coatings with 2–3 wt% ZrO₂ nanoparticles possess the best corrosion performance among the coating specimens [22]. And the ZrO₂ always have been used as thermal barrier for the excellent thermal stability, excellent chemical stability and low thermal conductivity [23,24], but rarely used in organic coatings to improve its thermal property. So in this article, with the aim that improving the thermal property and not decrease corrosion resistance of organic coatings, the ZrO₂ nanoparticles are joined to the electrophoresis coating. And effect of silane to the thermal property of magnesium alloy is also studied.

1. Experimental

1.1. Materials and solutions

Specimens of AZ31 Mg alloy (nominal composition: 2.5–3.5%Al; 0.7–1.3%Zn; 0.2–1%Mn; <0.05%Si; <0.01%Cu; <0.001%Ni; <0.002%Fe) received from Southwest Aluminum Goods Manufacture Company (China) are used for the different treatments. For cleaning, Mg panels are first immersed in a commercial alkaline cleaner bath at 65 °C for 30 min, then in a pickling solution bath with 192 g/l CH₃COOH and 50 g/l NaNO₃ at ambient temperature for 1 min.

Two kinds of the silane coupling agents (3-aminopropyl) diethoxymethyl silane (APS) and 3-glycidoxypolytrimethoxy silane (GPS), produced by Nanjing Capatue Chemical Com Ltd (China), are used in the study. Solutions with concentrations 2% silane are prepared 24 h before being applied.

For the E-coating, a commercial paint E11-96 with epoxy modified polyurethanes resin is from Institute of Southwest Engineering Technology.

The nano-ZrO₂ powder, about 20–40 nm, were bought from Xuan Cheng Jing Rui New Materials Com, Ltd. To modify nano-ZrO₂ powder's aggregation, the powder was ultrasonic dispersion with GPS solution at the ratio of 25 g/200 ml for 10 min, and then filtrated and dried at 100 °C for 1 h, ball milled again with some paint. At last they are dumped into the paint at the ratio of 25 g/1000 ml.

1.2. Silane film and E-coating preparation

The cleaned Mg panels are dipped in the APS silane solution for 30 s, then dried by hot air to get rid of the excess liquid, and finally cured in an oven at 100 °C for 30 min to ensure condensation siloxanes.

For the cathodic electrophoretic deposition, stainless steel plate was used as anode and Mg alloy panel as cathode. Three kinds of E-coating were prepared (Table 1), Mg alloy panel without silane film and the paint without nano-ZrO₂ powder (shorthand for E-coating), Mg alloy panel with silane film and the paint without nano-ZrO₂ powder (shorthand for silane + E-coating), and Mg alloy panel with silane film and the paint with nano-ZrO₂ powder (shorthand for E-coating + ZrO₂). The cathodic electrophoretic deposited at voltage 140 V for 2.5 min. After that, the panels are cleaned with DI-water and cured at 160 °C for half an hour.

1.3. Thermal shock test

The panels were put into the furnace at set temperature, and took out after 5 min, air cooling to room temperature, the operation repeated until six times or the coating damaged. There is an exception that the thermal shock test was air cooling once and then water cooling once, when E-coating + ZrO₂ samples was tested at 500 °C.

1.4. Machu experimental

The panels were cross-scribed on the surface and sealed at edge, and then immersed into a solution of 5% NaCl+0.6% H₂O₂ at 37 °C for 24 h. Then the solution was totally refreshed, and the panels were then taken out after immersing another 24 h. The tape was used to pull off the delaminated paints along the scribe lines.

1.5. DTA analysis

The DTA analysis is applied at the heating rate of 10 K/s in the air atmosphere, using WCR-2C microcomputer differential thermal analyzer made by Beijing optical instrument factory. And the test powder was scraped from the cured coating.

1.6. Microstructure examination and element analyze

The surface macro-morphologies were recorded with digital camera. The microstructure was sprayed carbon in order to

Table 1
Three kinds samples of E-coating.

Sample mark	Mg panel treatment method	
	Silane pretreatment	Electro-deposition with Nano-ZrO ₂
E-coating	No	No
Silane + E-coating	Yes	No
E-coating + ZrO ₂	Yes	Yes

be observed by ZEISS EVO18 scanning electronic microscope and FEI-Quanta 200 scanning electronic microscope. The element analysis was conducted by EDS attached on SEM. And the carbon was no calculation in the analysis results using ZEISS microscope for that the carbon is sprayed on coatings.

2. Results and discussion

2.1. Comparison of corrosion property

The corrosion resistance of coating can be rapidly evaluated by the Machu accelerated corrosion experiment. As shown in Fig. 1, the E-coating after 48 h machu experiment has been severely corroded and taken off (Fig. 1(a)), and the silane + E-coating corroded (Fig. 1(b)), but the coating has not been taken off. While the E-coating + ZrO_2 show the best corrosion resistance property (Fig. 1(c)). M. Behzadnasab [22] reported that silane can bond with OH groups on the surface of ZrO_2 nanoparticle, which increase the corrosion resistance of coating. At the same time, the silane pretreated on the AZ31 Mg alloy can also increase the corrosion resistance [14]. So the E-coating + ZrO_2 sample have the best corrosion resistance property.

2.2. Effect of silane on the thermal property

Fig. 2 is the morphology of the E-coating and silane + E-coating at different thermal shock conditions. The E-coating is uniform and smooth (Fig. 2(a)), and the morphology of silane + E-coating is similar with the E-coating. Both the E-coating and silane + E-coating show no blistering or damage after six thermal recycles from 350 °C to room temperature (Fig. 2(b) and (d)). However, obvious damage could be seen from both the E-coating and silane + E-coating after test at 400 °C (Fig. 2(c) and (e)).

The micro-morphology of E-coating samples and the element compositions of points after thermal shock test at different conditions are shown in Fig. 3 and Table 2. The surface of the E-coating is very smooth (Fig. 3(a)) and become rough after thermal shock 6 times at 350 °C. The coating was ablated, but not seriously, and still very complete which is also agree with its macro-morphology characteristics (Fig. 2(b)). Comparing its component to the coating before test, it can be found large numbers of Mg element in the coating and the oxygen element significantly decreased, that indicate that Mg element diffuse into the coating (Fig. 3 point 2). While it was damaged after air-cooling from 400 °C once, and the edge of breakage detach with Mg substrate (Fig. 3(c)). The component of peeling off area is mainly Mg and O (Fig. 3 point 3), and both the morphology and component of the E-coating after tested at 400 °C (Fig. 3 point 4) are very similar with the coating before test (Fig. 3 point 1).

Combining with the result of DTA (Fig. 4), it can be found the cured electrophoretic coating started to exothermic decomposition from 200 °C, drastic exothermic from 410 °C and reached an exothermic peak at 487 °C. It suggests that the

coating can stay at 400 °C and 350 °C for a short time without drastic decomposition.

According to the above, for the good temperature resistance, the E-coating could keep intact after thermal cycle 6 times at 350 °C. Though it was broken after cooling from 400 °C, the compositions and morphology of the unpeeling off electrophoretic coating after tested at 400 °C is very like the coating before test, that suggest the structure of the unpeeling off coating after is not much change with tested at 400 °C. so the damage of the coating after tested at 400 °C is not for organic decomposition, whose decomposition would lead to the structural damage at 400 °C, but mainly owe to the thermal stress.

Fig. 5 is the microphotograph of silane + E-coating at 350 °C and 400 °C after thermal shock test and the element compositions of points in it are shown in Table 3. It can be found that the macro-photographs of silane + E-coating and E-coating after tested at 350 °C both keep integrity (Fig. 2(b) and (d)). But there are some different between them in the microphotograph (Fig. 3(b) and Fig. 5(a)), a hole can be found in the silane + E-coating after thermal cycle 6 times at 350 °C (Fig. 5(a)), whose diameter is about 60 μm . The edge of the hole is intact and bonding with the Mg substrate, and its morphology is rough like the E-coating after tested at 350 °C (Fig. 3(b)). The component of the coating after tested at 350 °C was got by the EDS analysis (Fig. 5 pit 6), it can be found the component of the coating is very similar with the E-coating before thermal shock test, and the component of the hole is mainly Mg and O (Fig. 5 pit 5).

The hole formed in the silane + E-coating after thermal cycle at 350 °C may be result from that silane film can inhibit the formation of hydrogen at the cathode, and that increase compactness of the coating. So it has bigger thermal stress at the time of thermal shock that also can explain why more Mg element appear in the coating of E-coating than silane + E-coating after tested 350 °C, the more compactness, the harder thermal diffusion. The result also proves that the destruction of the coating is mainly for the thermal stress.

Though silane + E-coating sample was also damaged after heated at 400 °C and air cooling once, the edge of the broken off area is bonding with the Mg substrate together (Fig. 5(b)), which is different with E-coating sample after 400 °C (Fig. 2(c)). The component of the coating after thermal shock is very similar to the E-coating before test (Fig. 5 pit 8) too, and the component of the hole is almost Mg (Fig. 5 pit 8). And combining with the component and morphology of the coating before and after, the damage reason is also the thermal stress.

According to the literature [25], silane adhesion performance is related to the silicon hydroxyl number, and the number has a significant relationship with temperature, such as there is 5.3 silicon hydroxyl per nano-square at room temperature, 2.6 silicon hydroxyl at 400 °C, only one at 850 °C. So when the temperature is not very high, silicon hydroxyls condense into the Si—O—Si network, which have high rigidity, that improve the adhesion properties and the density of silane film. When the temperature is very high, much more rigid Si—O—Si are formed, that would make film rigidly and toughness decrease, the film is easily to be damaged, and show

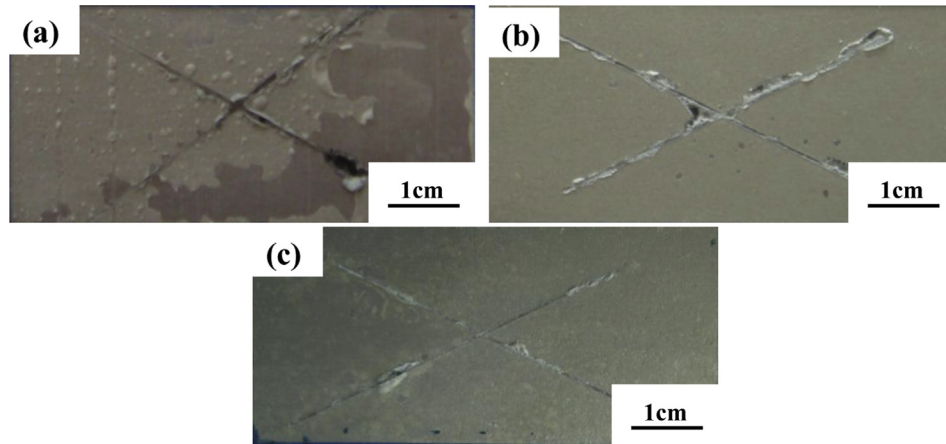


Fig. 1. The morphology of different coating after 48 h Machu experiment (a) E-coating sample (b) silane + E-coating sample (c) E-coating + ZrO_2 sample.

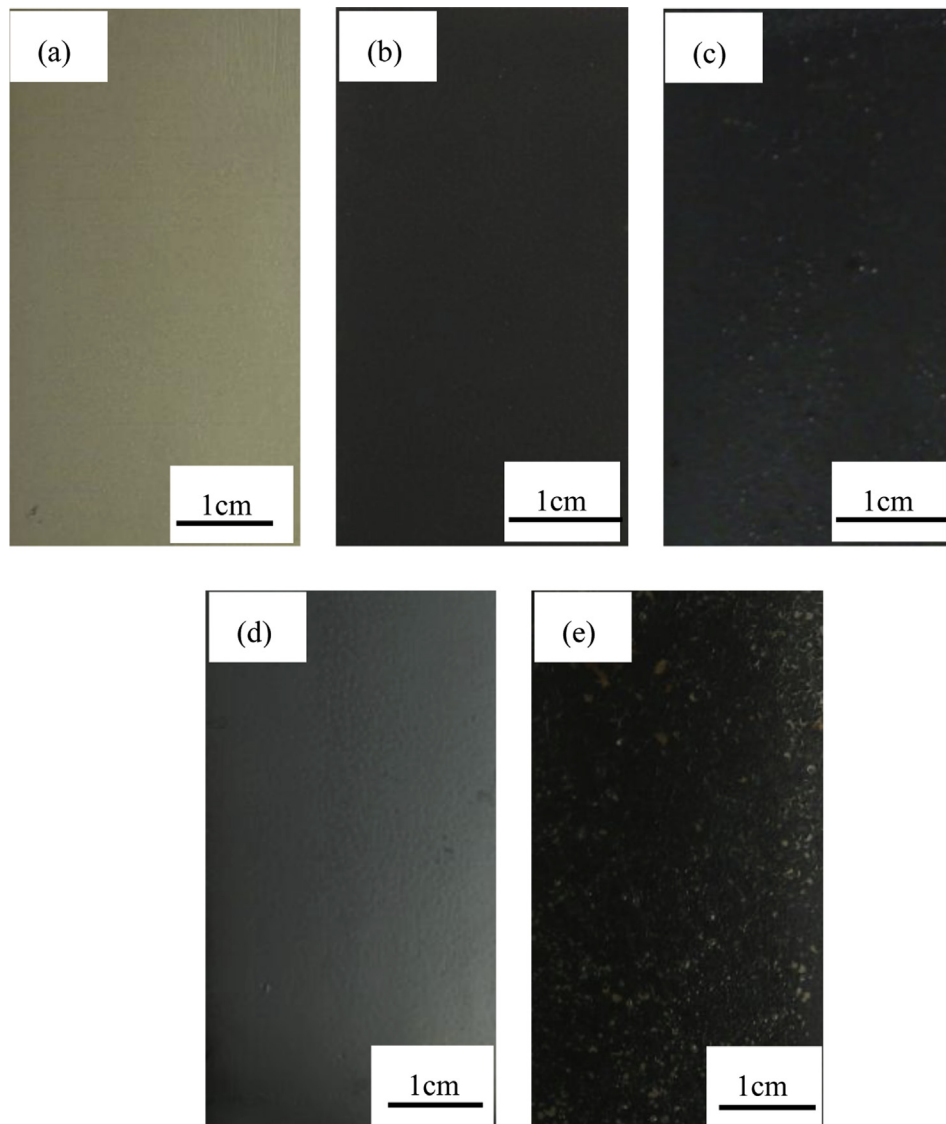


Fig. 2. The morphology of E-coating and silane + E-coating before and after thermal shock (a) E-coating before test (b) E-coating 6 times thermal recycle at 350 °C (c) E-coating heated at 400 °C then air cooling once (d) Silane + E-coating 6 times thermal recycle at 400 °C (e) Silane + E-coating heated at 500 °C then air cooling once.

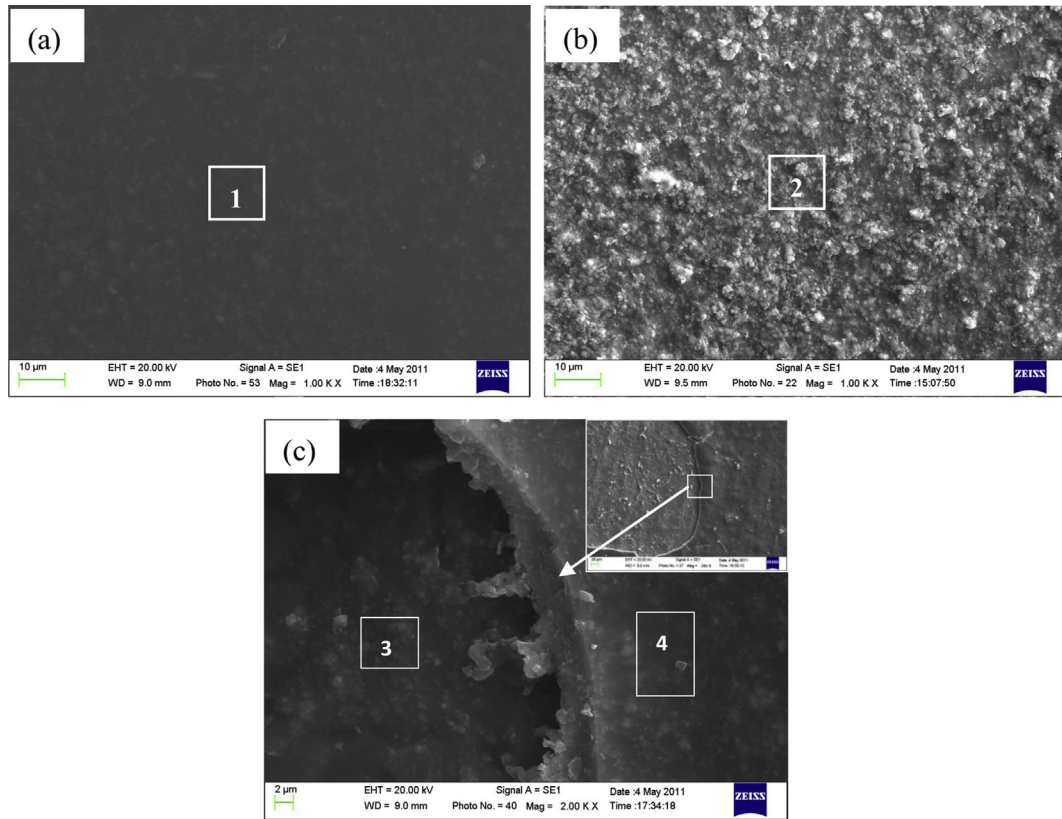


Fig. 3. The microphotograph of E-coating before and after thermal shock (a) the original coating (b) thermal cycle 6 times at 350 °C (c) heat at 400 °C and air cooling once, its macro-graphs is showed on the upper right-hand corner.

poor the adhesive performance. So silane can greatly improve the adhesive performance between the E-coating and Mg substrate even at 400 °C. That is why the edge of the broken off area is bonding with the Mg substrate together.

To sum up the above discussion, both the silane + E-coating and E-coating was damaged after the thermal shock test at 400 °C, but the edge of the broken off coating area was deferent, and the edge of the silane + E-coating is still bonding with the Mg substrate together, while the edge of the E-coating is separation with the Mg substrate. The component of coatings after thermal shock is similar to coatings before thermal shock. These show that the existence of the silane film can improve the coating thermal shock ability for the good adhesive performance between the E-coating and Mg substrate.

2.3. Effect of nano-ZrO₂ on the thermal property

Fig. 6 is the morphology of the E-coating + ZrO₂ before and after thermal shock. It can be found the surface of the

Table 2
Chemical compositions of points in Fig. 3(at %).

Point	O	Mg	Al	Si	Ti
1	60.25	—	4.73	26.86	8.17
2	51.49	21.22	4.45	17.71	5.13
3	19.83	71.87	2.58	4.93	0.79
4	59.8	—	4.15	28.14	7.91

Table 3
Chemical compositions of points in Fig. 5(at %).

Point	O	Mg	Al	Si	Ti
5	14.88	83.15	1.72	0.25	—
6	62.94	1.61	3.89	25.32	6.25
7	13.75	81.64	2.30	2.31	—
8	64.55	—	3.24	24.25	7.95

coating adding nano-ZrO₂ remain smooth and keep intact, even after test at 400 °C, this is very different with the coating without ZrO₂. And it was damaged when tested at 500 °C. So comparing to the coating without nano-ZrO₂ powder, the E-coating + ZrO₂ have better thermal resistance property.

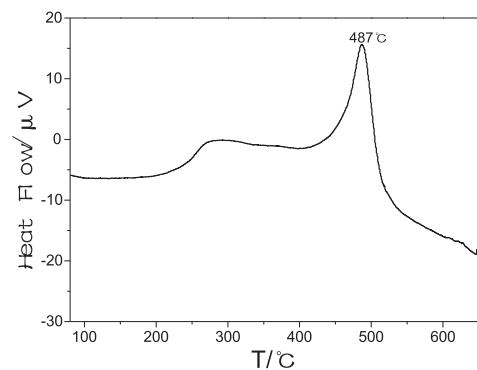


Fig. 4. DTA curve of the E-coating.

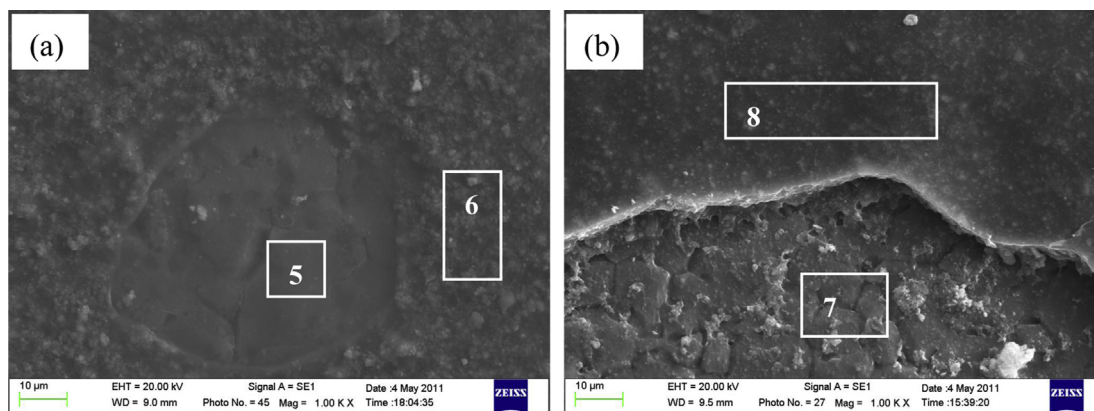


Fig. 5. Microphotograph of silane + E-coating at 350 °C and 400 °C after thermal shock (a) thermal cycle 6 times at 350 °C, (b) heated at 400 °C and air cooling once.

Fig. 7 is the micro-morphology of E-coating + ZrO_2 before and after thermal shock test at different conditions, it can be found many small white points with the Zr element is well distributed in the coating (Fig. 7(a)), and ZrO_2 was electrophoretic deposited in the coating. When it was tested at 400 °C for six times, there are some ablation in the coating after thermal shock, but not broken off, while the coating without ZrO_2 is damaged after tested at 400 °C (Fig. 3(c) and Fig. 5(b)). But the E-coating + ZrO_2 was damaged after thermal shock at 500 °C, and its micro-morphology (Fig. 7(c)) is similar to silane + E-coating after thermal shock at 400 °C (Fig. 5(b)), that the unbroken off coating is still bonding with the Mg substrate together and keep integrity. And its micro-morphology have not greatly change, comparing with E-coating + ZrO_2 before test (Fig. 7(c)), While the broken off area mainly be Mg element. So the thermal stress is also main factor for the damage of the coating.

From thermal shock test, it can be found that the thermal stability of the coating can be improved by adding nano- ZrO_2 powder treated by 3-glycidoxypyltrimethoxy silane (GPS).

The reason may be that the nanometer particles in reasonable amounts can increase the thermal stability of the coating [19,26], what the reason is may be that the inhibition of molecular mobility of polymer chains [27] and good thermal stability of these fillers [28], while the increased crosslinking density between the resin and nano- ZrO_2 by silane may be one of the factors [28].

In conclusion, thermal shock performance of coatings can be effectively improved by adding nano- ZrO_2 treated after silane pretreatment, that it can keep intact after thermal shock test 6 times at 400 °C, and damage at 500 °C mainly for the thermal stress.

3. Conclusion

Through the thermal shock experiment and Machu experiment, it is found that both the corrosion resistant and thermal shock resistant properties can be improved by modifying the Mg Specimen with APS silane, while the coating added nano-

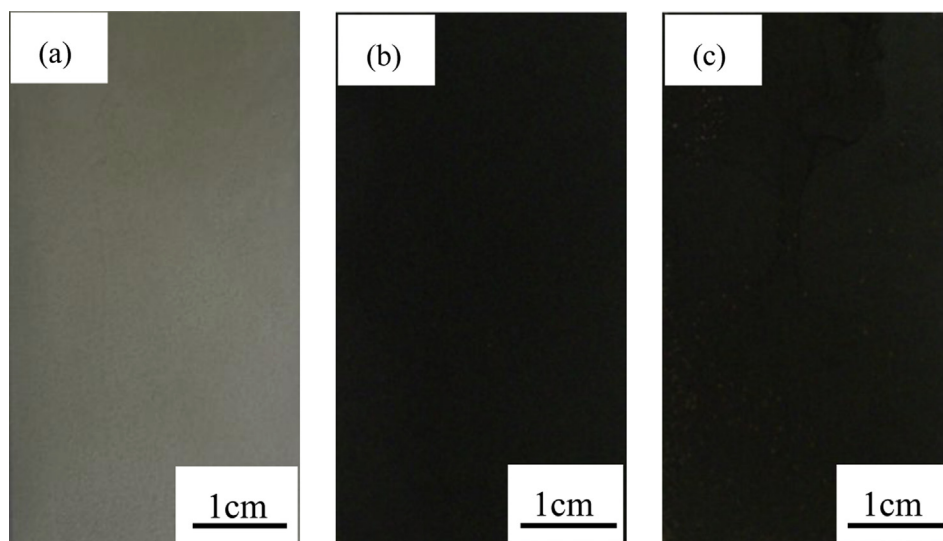


Fig. 6. The morphology of E-coating + ZrO_2 before and after thermal shock (a) before test (b) thermal cycle 6 times at 400 °C (c) after heated at 500 °C — cooled in air — heated at 500 °C — cooled in water.

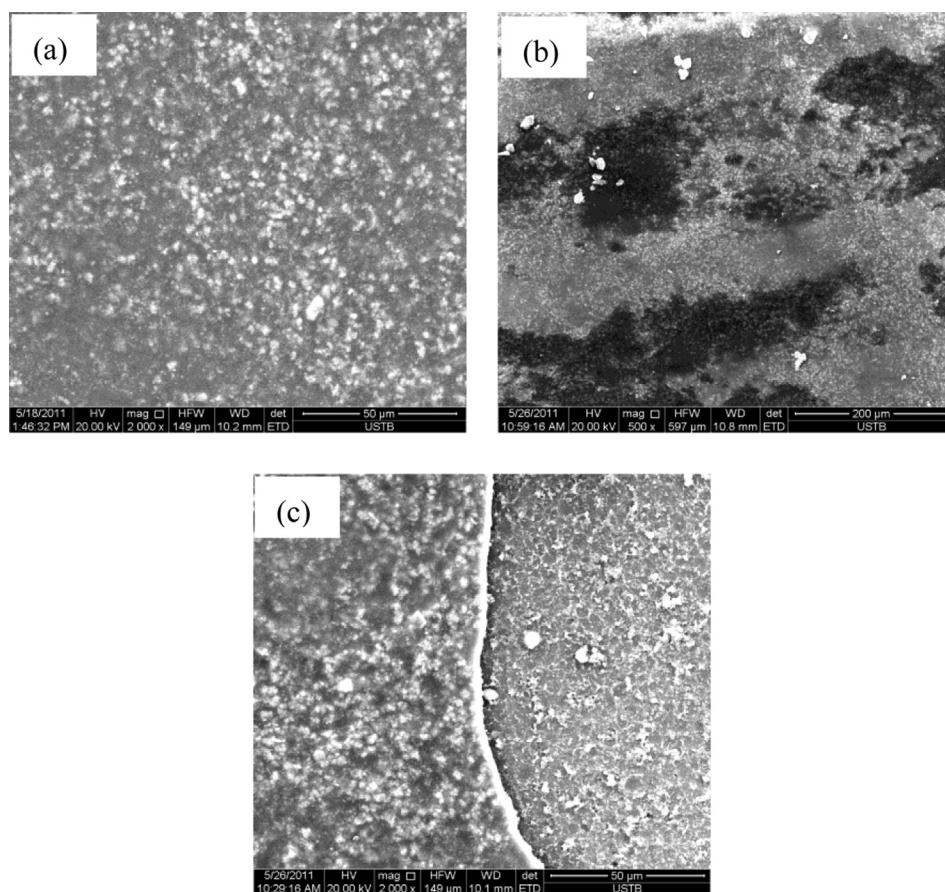


Fig. 7. The micro-morphology of E-coating + ZrO_2 samples heat treatment at different conditions (a) before test (b) thermal cycle 6 times at 400°C (c) after heated at 500°C – cooled in air- heated at 500°C – cooled in water.

ZrO_2 powder which is treated by GPS silane has the best thermal shock resistant and corrosion resistant property, even can be used at 500°C for a short time. And the results also show that the damage reason of the coatings after thermal shock at 400°C or 500°C is mainly due to the thermal stress, not the collapse of the coating.

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